which is one of the strongest oxidizing fluorinators[8] known. The applicability of the Lewis acid-activated F_2 system, however, seems to be limited to starting materials which themselves do not form stable adducts with the Lewis acid. The given examples demonstrate that the oxidizing power of fluorine can be promoted significantly by the simultaneous use of a strong Lewis acid and an energy source promoting dissociation of F_2 into $F\cdot$ atoms. Consequently, many reactions previously requiring the use of the prohibitively expensive PtF_6 may now be carried out at a reasonable expense by the use of Lewis acid promoted activated fluorine.

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Registry No. F_2, 7782-41-4; NF_3, 7783-54-2; SbF_5, 7783-70-2; AsF_5, 7784-36-3; BF_3, 7637-07-2; $NF_4^+AsF_6^-$, 16871-75-3; $NF_4^+BF_4^-$, 15640-93-4.

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Bis(fluorosulfato)bromates(I) of Lithium and Sodium

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Chung and Cady[1] have shown that the solid compound, cesium bis(fluorosulfato)bromate(I) [$CsBr(SO_3F)_2$] is produced when $BrSO_3F$ combines with $CsSO_3F$ and have found qualitative evidence that a single fluorosulfate ion, when introduced into liquid bromine(I) fluorosulfate, probably becomes associated with more than one molecule of $BrSO_3F$. Quereshi and Aubke[2] have confirmed the existence of $CsBr(SO_3F)_2$ and have reported its Raman spectrum.

In the present study solutions of the fluorosulfates of Li, Na, K, Rb, or Cs in excess bromine(I) fluorosulfate were subjected to dynamic vacuum at room temperature. In each case the removal of $BrSO_3F$ left behind a liquid more viscous but less highly colored than pure liquid bromine(I) fluorosulfate. As evaporation occurred a solid phase appeared. For the systems involving potassium or rubidium, the solid which formed was KSO_3F or $RbSO_3F$, respectively. For systems involving lithium or sodium, the solids which first formed were $LiBr(SO_3F)_2$ or $NaBr(SO_3F)_2$.

Experimental Section

System $NaSO_3F$-$BrSO_3F$. A mixture of $NaSO_3F$ (2.233 mmol) and $BrSO_3F$ (30.06 mmol) was held in a glass vessel at 90° for 1.5 hr and was later subjected to dynamic vacuum at about 23° to remove $BrSO_3F$. At first the vessel lost weight rapidly, but the rate of loss decreased greatly after the ratio of $BrSO_3F$ to $NaSO_3F$ fell below 2:1. Much solid was then present, but the material obviously was partially liquid down to a ratio of 1.4. Possibly liquid was present down to a ratio of about 1.0. Pumping was continued until the weight of the residue fell to 0.6870 g, corresponding to a molar ratio of $BrSO_3F$ to $NaSO_3F$ of 1.04. During the last part of the pumping operation, the solid was not homogeneous in color. Some parts were much darker than others. The Raman spectrum of one nearly white region contained lines characteristic of $NaSO_3F$. When the flask was then held at 65° for 18 hr, but with no pumping, the solid became homogeneous and was pale yellow. The Raman spectrum of $NaSO_3F$ was no longer found and the spectrum was much like that for $CsSO_3F\cdot BrSO_3F$. Raman spectra taken with the laser beam directed at several random locations in the homogeneous 1:1 solid were identical.

Table I. Raman Spectra for $MBr(SO_3F)_2$ Salts

$LiBr(SO_3F)_2$		$NaBr(SO_3F)_2$		$CsBr(SO_3F)_2$	
ν, cm^{-1}	Intens[a]	ν, cm^{-1}	Intens[a]	ν, cm^{-1}	Intens[a]
				40	6.2
				69	24.2
96	16.2				
124	8.2	108	13.8	109	12.8
		(174)	6.9	(182)	1.2
246	100	263	51.4	262	100
412	3.1	398	3.5	399	1.2
446	55.8	443	44.1	437	42.8
557	7.5	554	5.9	557	3.1
583	6.2	578	11.0	573	3.1
626	48.7	624	100	617	79.4
803	12.2	827	14.8	778	2.5
1062	6.9	1023	0.9	1018	1.9
1280	8.5	1238	22.3	1220	13.2
1339	5.5	1379	7.3	1373	7.2
		1395	10.8		

[a] Uncorrected Raman intensities; ( ) probably an impurity.

Analysis. The salt was allowed to react with aqueous sodium hydroxide solution. Sulfur was then determined gravimetrically as $BaSO_4$ and bromine as AgBr. Fluorine was determined by titrating with thorium nitrate solution and the end point was observed with the help of an Orion fluoride-ion-selective electrode. *Anal.* Calcd for $NaSO_3F\cdot BrSO_3F$: S, 21.3; Br, 26.5; F, 12.6. Found: S, 22.6; Br, 25.7; F, 12.7.

System $LiSO_3F$-$BrSO_3F$. Bromine(I) fluorosulfate (25.5 mmol) was mixed with dry lithium fluorosulfate (4.543 mmol) in a glass vessel. While this 5.61 to 1 mixture was held at 65° for 1.5 hr, it was completely liquid. As it cooled to room temperature, part of the material crystallized. The system was then subjected to dynamic vacuum at about 23° with $BrSO_3F$ distilling away. Although the rate of removal of $BrSO_3F$ decreased somewhat when the ratio of $BrSO_3F$ to $LiSO_3F$ fell below about 3 to 1, the rate remained higher than for the systems involving $NaSO_3F$ and $CsSO_3F$. As $BrSO_3F$ was removed, one could easily see a liquid phase down to a molar ratio of about 1.9, and the solid continued to look wet down to a ratio of about 1.3. After the molar ratio of $BrSO_3F$ to $LiSO_3F$ had fallen to 1.02, pumping was stopped and the mixture was allowed to stand for 5 days. The resulting solid was a homogeneous pale yellow, dry, flaky material which had a Raman spectrum resembling those of $CsSO_3F\cdot BrSO_3F$ and $NaSO_3F\cdot BrSO_3F$. No bands attributable to $LiSO_3F$ were observed. *Anal.* Calcd for $LiSO_3F\cdot BrSO_3F$: S, 22.5; Br, 28.0; F, 13.3. Found: S, 23.4; Br, 27.6; F, 13.0.

Spectra. Raman spectra were recorded using the 5145-Å exciting line of a Coherent Model 52 Ar-Kr ion laser in conjunction with a Spex 1401 double monochromator and a thermoelectrically cooled F.E.-130 phototube. The observed spectra are reported in Table I.

^{19}F nmr spectra of solutions of alkali metal fluorosulfates in $BrOSO_2F$ were obtained using a Varian Associates Model V-4311 nmr spectrometer at 56.4 MHz. The samples were sealed in 5-mm Pyrex glass tubes, and trichlorofluoromethane was used as an external standard. All of the samples gave only a single "line" spectrum. The chemical shift was somewhat dependent upon concentration and decreased as the ratio $BrSO_3F:MSO_3F$ became smaller. The chemical shift observed for pure bromine(I) fluorosulfate was −34.9 ppm. For the solutions the values ranged down to −37.9 ppm. Apparently exchange occured so rapidly that only one line was obtained for each solution. As the temperature was lowered, the line became so broad below about −45° that the "peak" disappeared.[3]

Discussion

The above experiments clearly indicate the existence of the new solid compounds $LiBr(SO_3F)_2$ and $NaBr(SO_3F)_2$. The materials appear to be homogeneous and have characteristic Raman spectra similar to that of $CsBr(SO_3F)_2$. Since lines for MSO_3F are lacking and since the ratio of $BrSO_3F$ to

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(1) C. Chung and G. H. Cady, *Z. Anorg. Allg. Chem.*, **385**, 18 (1971).

(2) A. M. Quereshi and F. Aubke, *Inorg. Chem.*, **10**, 1116 (1971).

(3) W. M. Johnson, Thesis, University of Washington, 1971.

MSO_3F is 1:1, the solids are best described as $LiBr(SO_3F)_2$ and $NaBr(SO_3F)_2$. The anion, $Br(SO_3F)_2^-$, is responsible for the yellow color of the salts.

When one attempts to obtain the corresponding salt of potassium or rubidium by evaporating $BrSO_3F$ from a solution containing dissolved potassium or rubidium fluorosulfate, the solid which crystallizes from the solution is KSO_3F or $RbSO_3F$. This does not mean that the $Br(SO_3F)_2^-$ is absent from the liquid phase. The close similarity of Raman spectra for the liquid solutions of fluorosulfates of all the alkali metals in $BrSO_3F$ suggests that all contain similar species. Apparently the solubility relationships favor crystallization of the fluorosulfate in two cases and of the bis(fluorosulfato)-bromate(I) in three cases.

The relatively slow rate of removal of $BrSO_3F$ from solutions having a $BrSO_3F$:MSO_3F molar ratio greater than 1 indicates some interaction. A comparison of the pumping rates indicates that cesium fluorosulfate causes the greatest reduction in volatility of the solvent while lithium fluorosulfate causes the least.

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Registry No. $NaSO_3F$, 14483-63-7; $BrSO_3F$, 13997-93-8; $LiSO_3F$, 13453-75-3; $LiBr(SO_3F)_2$, 40813-81-8; $NaBr(SO_3F)_2$, 40813-82-9.

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Preparation and Properties of Bromochlorofluorophosphine and Improved Syntheses for Dimethylaminochlorofluorophosphine and Dimethylaminobromofluorophosphine

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Dimethylaminobromofluorophosphine, $(CH_3)_2NPFBr$, was first prepared in 1968 by Clune and Cohn[1] using the reaction between F_2PNR_2 and BrCN; the equation is

$$2(CH_3)_2NPF_2 + BrCN \rightarrow (CH_3)_2NPF_3CN + (CH_3)_2NPFBr$$

The two products could not be separated by distillation; chromatographic techniques were required. For this reason, the procedure cannot be recommended as an effective synthetic route to the compound $(CH_3)_2NPFBr$.

The related chloro compound, $(CH_3)_2NPFCl$, was described by Roesky in 1969[2] as one of the products of the reaction between $(CH_3)_2NPCl_2$ and SbF_3. Reported yields were low (6.3%). In recent studies carried out in this laboratory, the compounds $(CH_3)_2NPFX$ (X = Cl or Br) have been synthesized in good yields (above 80%) and in high purity by methods described herein. The ready availability of these compounds has made it possible to synthesize, isolate, and characterize the formerly unavailable compound PFClBr.[3]

Synthesis of $(CH_3)_2NPFX$. The compound $(CH_3)_2NPFX$, where X = Cl or Br, has been prepared by two general reactions. (a) The first synthesis is based on the equation

$$[(CH_3)_2N]_2PF + 2HX \rightarrow (CH_3)_2NPFX + [(CH_3)_2NH_2]^+X^-$$

In this process, the ratio of HX to $[(CH_3)_2N]_2PF$ is critical. With a ratio of four HX to one $[(CH_3)_2N]_2PF$, PFX_2 is the major product.[4] If, however, the ratio is held to two HX per fluorophosphine, the compound $(CH_3)_2NPFX$ (X = Cl or Br) can be prepared in yields of about 85%. The process is effective for the chloro compound; however, it is difficult to separate $(CH_3)_2NPF$*Br* from any unreacted $[(CH_3)_2N]_2PF$ by fractional distillation. (b) The second synthesis is based on the equation

$$2(CH_3)_2NH + PFX_2 \rightarrow (CH_3)_2NPFX + [(CH_3)_2NH_2]^+X^-$$

The PFX_2 needed as a reactant is easily prepared by the action of an excess of HX on $[(CH_3)_2N]_2PF$. Amines such as piperidine and alkylated piperidines have also been used in this process in place of dimethylamine.[5]

While the first process (a) is more direct and is somewhat simpler than the second one (b), it is more difficult to separate the products and reactants of (a) through vacuum line distillation. On the other hand, the reaction between PFX_2 and the secondary amine gives the desired product in an easily purified form and in high yield. If a pure product is desired, the second process involving PFX_2 is recommended.

Synthesis and Properties of PFClBr. The compound PFClBr can be made by the reaction

$$(CH_3)_2NPFCl + 2HBr \rightarrow PFClBr + [(CH_3)_2NH_2]^+Br^-$$

The new compound melts at −122° and appears as a liquid at −120°, but its vapor pressure and boiling point could not be determined accurately because of increasing disproportionation with an increase in temperature. The pertinent equation is

$$2PFClBr \rightarrow PFCl_2 + PFBr_2$$

The ^{19}F nmr spectrum of PFClBr (dissolved in $CFCl_3$ at −40°) shows the expected doublet (J_{PF} = 1300 Hz, δ 64.6 ppm from $CFCl_3$). Small doublets for $PFCl_2$ (J_{PF} = 1320 Hz, δ 57.5 ppm from $CFCl_3$) and $PFBr_2$ (J_{PF} = 1300 Hz, δ 72.2 ppm from $CFCl_3$) also appeared as a result of the disproportionation process. The ^{31}P nmr spectrum of PFClBr dissolved in TMS also displayed the expected doublet (J_{PF} = 1300 Hz, δ −233 ppm from 85% H_3PO_4) along with small doublets for $PFCl_2$ and $PFBr_2$. The infrared spectrum of PFClBr shows absorptions assigned to the P-F stretch at 840 cm^{-1}, to the P-Cl stretch at 515 cm^{-1}, and to the P-Br stretch at 421 cm^{-1}. Delwaulle and Francois[3] had assigned Raman lines in a mixture of $PFBr_2$ and $PFCl_2$ to PFClBr although no separation of the product was achieved. Their assignments are ν_{P-F} 822 cm^{-1}, ν_{P-Cl} 500 cm^{-1}, and ν_{P-Br} 415 cm^{-1}. The mass spectrum shows a very strong parent peak at m/e 166. This is assigned to $PF^{37}Cl^{79}Br^+$ and to $PF^{35}Cl^{81}Br^+$. Other peaks are listed in the Experimental Section. The foregoing instrumental data leave no reasonable doubt as to the identity of PFClBr.

Nmr Correlations. (a) Fluorine-19 Resonance. The chemical shift values for ^{19}F nmr spectra in the series $(CH_3)_2NPFX$ are as follows: X = F, δ 66 ppm; X = Cl, δ 69.5 ppm; X = Br, δ 75.6 ppm (all measured from $CFCl_3$). The shield-

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[1] J. E. Clune and K. Cohn, *Inorg. Chem.*, 7, 2067 (1968).

[2] H. W. Roesky, *Inorg. Nucl. Chem. Lett.*, 5, 891 (1969).

[3] The compound PFClBr has never been isolated as a distinct species although M. F. Delwaulle and F. Francois, *Acad. Sci.*, 223, 796 (1946), reported seeing its Raman spectrum in a mixture of $PFBr_2$ and $PFCl_2$.

[4] J. G. Morse, Doctoral Dissertation, University of Michigan, 1966.

[5] R. G. Montemayor, Doctoral Dissertation, University of Michigan, 1970.